Experimental report

10/03/2017

Proposal:	**5-31-2481**	**Council:**	4/2016
Title:	Study of the nuclear and magnetic structure of the novel multiferroic(YMn_3)Mn_4O_{12}		
Research area:	Materials		

This proposal is a new proposal

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Samples: YMn_7O_{12}

Instrument	Requested days	Allocated days	From	To
D20	2	2	28/09/2016	30/09/2016

Abstract:

We propose a powder neutron diffraction study of the nuclear and magnetic structure of the new quadruple perovskite $YMn_3Mn_4O_{12}$ which displays a remarkable magnetic ferroelectric behaviour, similar to $CaMn_3Mn_4O_{12}$ and $LaMn_3Mn_4O_{12}$. As compared to the latter compounds, $YMn_3Mn_4O_{12}$ exhibits significantly higher antiferromagnetic ordering temperatures, T(N,B)=108 K and T(N,A')=65 K, corresponding to the ordering of the B- and A'-sites, respectively, and an unexpected second-order phase transition at T*=202 K. These features prompt us to investigate the changes of the nuclear and magnetic structure across these transitions. Favourable conditions of the proposed study are the limited structural distortions inherent of the quadruple perovskite structure and the single-valent Mn(3+) characteristics of $YMn_3Mn_4O_{12}$. We expect that the results obtained shall unveil clear correlations between the magnetic structure and the structural changes induced by the magnetic orderings, thus providing a hint as to the microscopic mechanism of spin-lattice coupling in magnetic ferroelectric and, specifically, the controversial role of the exchange striction and of the Dzyaloshinsky-Moriya interaction.

Experimental report of proposal 5-31-2481:
Study of the nuclear and magnetic structure of the novel multiferroic $(YMn_3)Mn_4O_{12}$

Objective and expected results: The purpose of this experiment was to study the nuclear and magnetic structure of a novel magnetic multiferroic (MF), $(YMn_3)Mn_4O_{12}$, characterised by the quadruple perovskite structure $(AA'_3)B_4O_{12}$ and previously obtained under HP/HT conditions. $(A\mathrm{Mn}_3)\mathrm{Mn}_4\mathrm{O}_{12}$ compounds are very promising MF's where exchange striction is expected to play a dominant role. Notable is the large polarisation $\sim 0.26\mu\mathrm{C\ cm}^{-2}$ in $(CaMn_3)Mn_4O_{12}$ and even larger values $\sim 0.7\mu\mathrm{C\ cm}^{-2}$ were recently observed by some of us in $(LaMn_3)Mn_4O_{12}$ polycrystals. Values in the $1-10\mu\mathrm{C\ cm}^{-2}$ range relevant to applications can be expected in single crystals or epitaxial films. The motivation is that the distortion of the quadruple perovskite structure is simpler than that of the ABO_3 perovskites due to the high symmetry of the oxygen sites. We therefore expect to observe directly the structural changes at the AFM ordering temperature, T_N, by diffraction methods, thus enabling us to study the possible magnetostrictive phenomena. A promising indication is given by a previous study on $(LaMn_3)Mn_4O_{12}$, where the lattice parameters of the $I2/m$ structure display an anomaly at T_N. As compared to the latter compound, notable features of $(YMn_3)Mn_4O_{12}$ were reported to be significantly higher AFM ordering temperatures, $T_{N,B}$=108K and $T_{N,A'}$=65K, that we supposed initially to be associated with the magnetic ordering of the B and A' sites, respectively, and a further phase transition at T*=200K of unknown origin detected both in specific heat and magnetisation measurements.
Specific objectives of the proposal were as follows: (i) to unveil the nature of the transition at T^*, which is unexpected in the $(A\mathrm{Mn}_3)\mathrm{Mn}_4\mathrm{O}_{12}$ system. (ii) to determine the magnetic structures at $T_{N,B}$=108 K and $T_{N,A'}$=65 K. (iii) to detect possible structural changes occurring in the ferroelectric phase below $T_{N,A'}$=65K.

Measurements performed: The experiment was successfully performed on 920 mg of powder as a function of temperature at the D20 beamline, with two different wavelengths λ_1=1.54 Å and λ_2=2.41 Å using a 90° take-off set up and a constant warming rate of 0.25 K/min from 2K to room temperature. The two wavelengths were chosen for an accurate determination of the nuclear and magnetic structure, respectively.

Results (i) The structural refinement of nuclear and magnetic structure were performed with Fullprof using the sequential and multi-pattern mode implemented in winPLOTR. The neutron data were successfully refined in the monoclinic I2/m space group in the whole 3.5-284K range. Evolution of the cell parameters and unit cell volume as a function of temperature are reported in figure 1. As expected at T*=200K, an anomaly of the cell parameters is detected, characterized by an increase of the unit cell volume of $\sim$ 0.1%. Based on these data, the presence of a second order transition is hypothesized at T*=200K but no change of space group was evidenced. Below T$\sim$ 110 K, the cell turns back into a normal evolution with decreasing temperature.
(ii) The evolution of diffraction patterns as a function of temperature shows one magnetic transition at 108K characterized by the increase of intensity on top of four nuclear Bragg peaks (110), (-211), (-121) and (121) as shown on figure 2. No additional peak were observed so we suppose the magnetic structure to be described by the wavector k=(0,0,0).
(iii) Below 65 K, the absence of anomalies in the diffraction patterns indicates that no coherent long-range magnetic phenomena occur at this temperature.

Conclusion The experiment was successfull. Indeed, it permited to reach our objectives: (i) We indentified the structural nature of the previously unknown transition at T*=200K by evidencing a strong anomalous behavior of cell parameters. (i) We resolved the magnetic structure of B-sites occuring at the high Néel température $T_{N,B}$=108K (iii) We reported the absence of orientation of A' sites at T=65K.

Participants: Marine Verseils (main proposer), Francesco Mezzadri (co-proposer), Davide Delmonte (co-proposer) and Laurent Chapon (local contact)

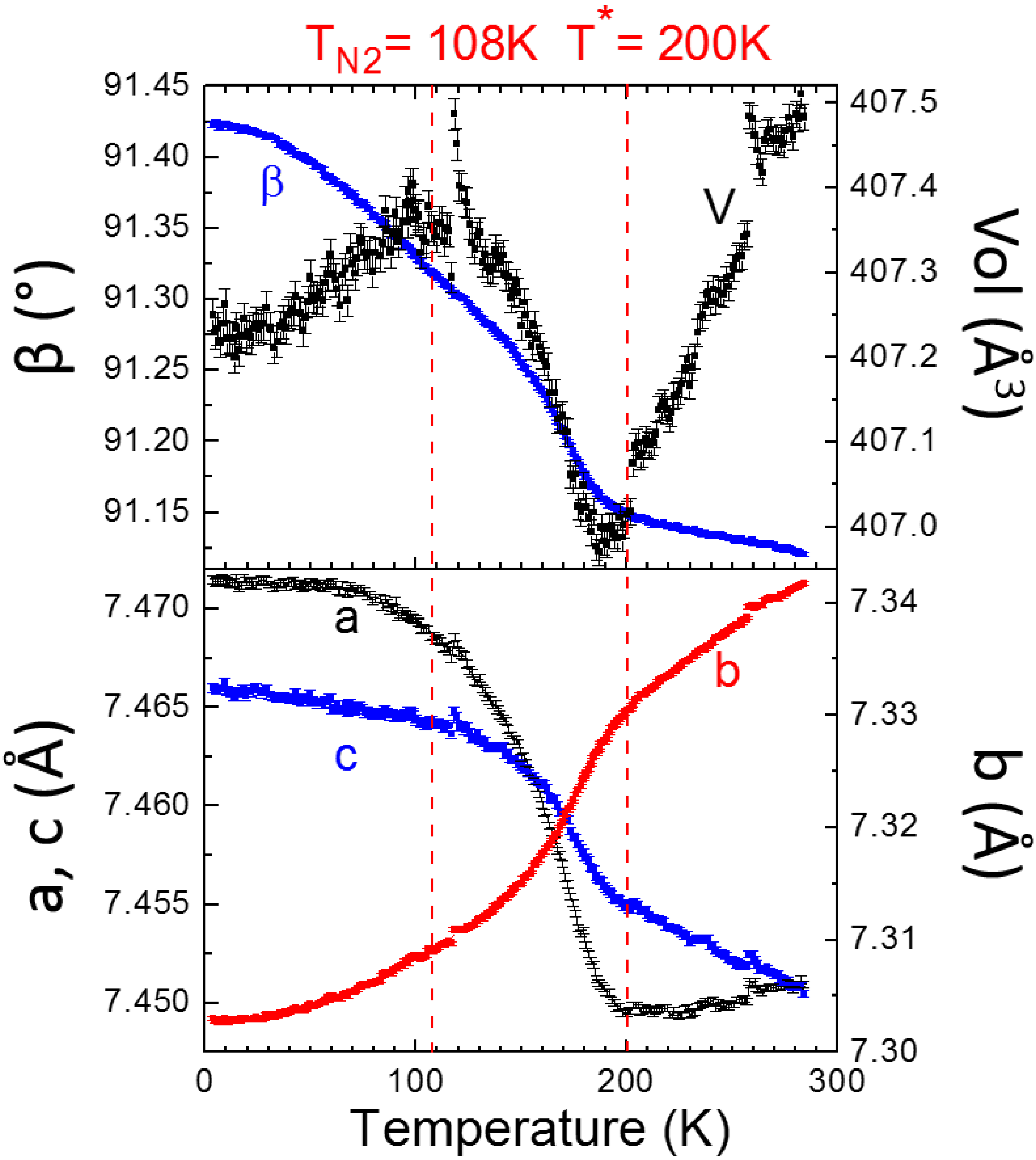

Figure 1: Lattice parameters (a, b, c and β) and unit cell volume (V) of $(YMn_3)Mn_4O_{12}$ as a function of temperature. Broken lines indicated the beginning and the end of the anomalous behavior.

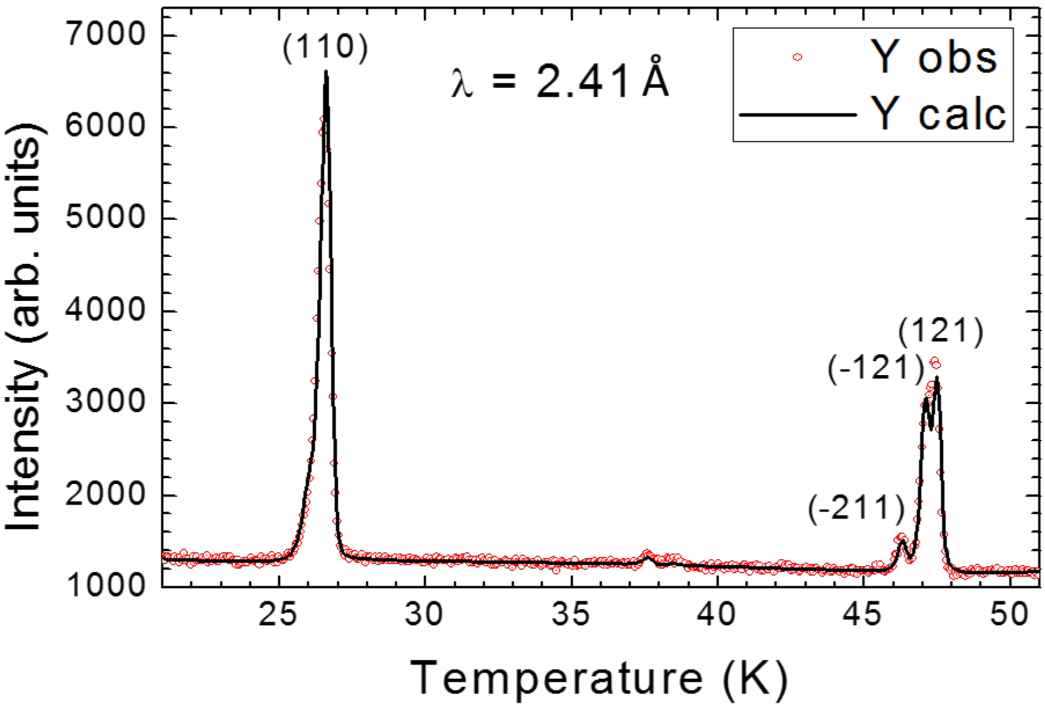

Figure 2: Red circles: Magnetic Bragg peaks of $(YMn_3)Mn_4O_{12}$ measured at 3.7 K using a neutron wavelength of 2.41 Å. Black line: result of refinement of the nuclear and magnetic structure of B-sites obtained with fullprof.